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TRANSLATION

CATALYTIC ACTIVITY OF ORGANIC POLYMERS
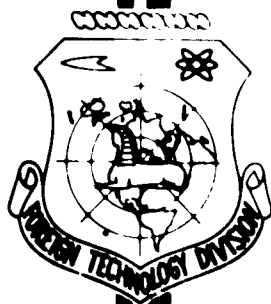
By

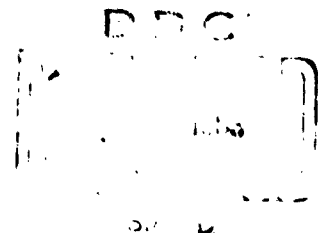N. P. Keyer, G. K. Boreskov, et al.

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CATALYTIC ACTIVITY OF ORGANIC POLYMERS

BY: N. P. Keyer, G. K. Boreskov, et al.

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Catalytic Activity of Organic Polymers

III. Law of Catalyzing on Chelate Polymers of Various Chemical Composition
and Structure

by

N. P. Keyer, G. K. Boreskov, L. F. Rubtsova and Ye. G. Rukhadze

The laws governing catalytic activity of polychelates of various metals, differing in composition of addenda atoms connected with the metal in the chelate unit, were investigated. It was revealed, that catalytic activity is determined by the metal, included in the chelate unit, nature of atoms, connected with the metal, and the nature of organic radicals in the polymer. Monomeric analogues of a number of polymers are catalytically inactive. No relationship was discovered between catalytic activity and electric conductivity.

The great breach, existing between natural metalloorganic catalysts - ferments of oxy-redux processes and the inorganic catalysts used by industry, compells to search for ways of creating new type of catalysts, which will be close in their properties to ferments. Oxidation-reduction ferments appear to be complex metalloorganic substances, having the polymeric albumin part. At present time for many ferments was established (by the IKS and other methods), that metal is connected with albumin - ligand with the aid of a chelate bond with its active groups (e.g. amino-and carboxyl groups of amino acids [1]).

The first results from studying catalytic activity of polychelates, obtained by us, point toward a high catalytic   activity and high selectivity in the action of similar polymers [2].

The purpose of this investigation was a   broader examination of laws governing catalytic activity in relation to the chemical composition of atoms, connected with the metal in the chelate joint, and also to compare catalysis over chelate polymers and chelate complex compounds, which appear to be   monomeric analogues of

chelate polymers.

The structure of chelate polymers in general view can be presented by the follo-

wing scheme

$$\ldots-\left[-R-L\left\langle{\scriptstyle X\atop Y}\right\rangle Me\left\langle{\scriptstyle Y\atop X}\right\rangle L-\right]_n -R-L-\ldots \quad (1)$$
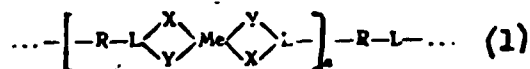
where X and Y - atoms of addenda ,included in the chelate joint and forming a donor-

acceptor bond; - L - R - organic ligands.

We investigated catalytic properties of polychelates,obtained on the basis of

ligands with different X and Y atoms. Polychelates with identical composition of

addenda atoms in the chelate unit were designated by us further on by one number (see

table 1).

We investigated polychelates of copper, nickel, cobalt, iron, zinc, cadmium,man-

ganese and palladium. Into the basic chain of polychelates were introduced radicals

of aliphatic and aromatic series R. In addition in polymers of certain structures

was changed the composition of organic groups g in the side chains. The structure and

composition of the investigated chelate polymers are described in table 1.

Table 1.Investigated chelate polymers,their chemical composition and structure

(1) Designation of polychelate	(2) Organic comp.on the basis of which chelate was derived	(3) Structure of chelate unit and abbrevia- ted designa- tion.	(4)Structure of monomeric link of polychelate
1 (R)e	Bis-disodiumthiacarbamate		Molecular weight 40000- 70000
2a R,r)	alpha-thioal ilamide(di- phenyl,tolidine,dianizidine) pyridine		(See page 3a for table 1)
2b(R)	Poly-4,4'-bis-alpha-thio (amidodiphenyl,tolidine,di anizidine)-2,6-lutidine. R-the same as in structure 2a		

2c   Rubianohydrogen acid

3a (r) Schiff basis 5,5-methylene-bis
    -salicylic aldehyde (4)

3b(r) Schiff basis diacetylresorcin

(r-the same as in structure 3a)   (See page 3a for Table 1)

3c(r) Schiff basis 5,5'-diasodiphenylene-
bis-salicylic aldehyde

(r - the same as in structure 3a)

4a 5,5'-methylene-bis-salicylic al-
  dehyde (5)

4b   Dinitrosoresorcin

4c   Trinitrosoflucroglucine
       (phloroglucinol)

* in polychelates of given structure the copper is monovalent

        1. Catalytic Activity of Polymers of the structure bis (aza-thia)
           with Chelate unit 2 (N_2S)Me.

     As was shown in table 1 we investigated three types of polymers of given struc-

ture, obtained on the basis of thioamides of alpha-picoline with diamines:

Table 1

(1)	(2)	(3)	(4)
	Бис-дитиокарбамат натрия (?) Na—S—S—NH—R—NH—S—S—Na $R_0 = -(CH_2)_3-$, $R_0 = -(CH_2)_6-$; $R_1 = \bigcirc$; $R_2 = \bigcirc\bigcirc$	2(S,S)Ni	Молекулярный вес 40 000—70 000
	о-Токил азамидо (дифения, толидин, дианизидин) пиридин $r_1 = H$; $r_2 = -CH_3$; $R_0 = \bigcirc\bigcirc$; $R_0 = \bigcirc\bigcirc$; $R_0 = \bigcirc\bigcirc$	2(N,S)Ni	
	Поли-4,4'-бис-о-тио(амидодифенил, толидин, дианизидин)-2,6-лутидин (R— те же, что и в структуре 2а)		
	Рубиановодородная кислота		
	Основание Шиффа 5,5-метилен-бис-салицилового альдегида (?) $r_1 = 2H$; $r_2 = -(CH_2)_2-$; $r_3 = -(CH_2)_3-$;	2(N,O)Ni	Молекулярный вес 40 000—100 000
	Основание Шиффа диметилрезорцина (r — те же, что и в структуре 2а)		Молекулярный вес 10 000
	Основание Шиффа 5,5'-диазодифенилен-бис-салицилового альдегида (r — те же, что и в структуре 2а)		
	5,5'-метилен-бис-салициловый альдегид (?)	2(О,О)Ni	
	Диметилрезорцин		
	Тринитрорезорцин		

benzidine, o-tolidine and o-dianisidine. The mentioned polymers are distinguished by the radical R in the basic chain and are designated later on as 2a $(R_5,r_1,)$ Me; 2a $(R_6, r_1,)$ Me and 2a $(R_7,r_1,)$ Me respectively. In this group of polymers for the convenience of designating are included polychelates, obtained on the basis of thioamides 2,6-lutidine with the very same diamines,differing from previous polymers by the presence of CH_3 group in the side chain (see table 1.) and designated by us as 2a (R_5,r_2')Me, 2a (R_6,r_2')Me and 2a (R_7,r_2') Me. In polymers of the 2a structure the nitrogen coordinately connected (bound) with the metal, is included in the pyridine ring. The second type of 2bMe polymer with the very structure of chelate unit $2(N,S)$ Me was obtained on the basis of polythioamido 2,6-lutidine with above mentioned diamines.
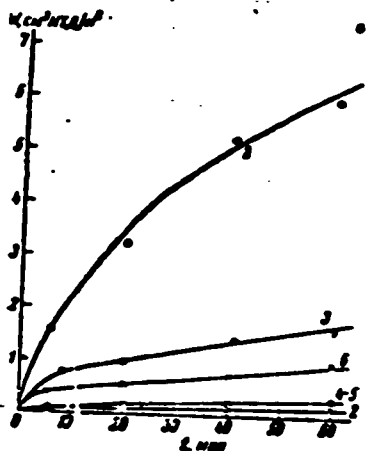

Fig.1.Kinetic isotherms of hydrazine decomposition into bis (aza-thia) polychelates of copper of different structure,distinguished by the composition of radicals ($T=108°$,p = 1 mm Hg):
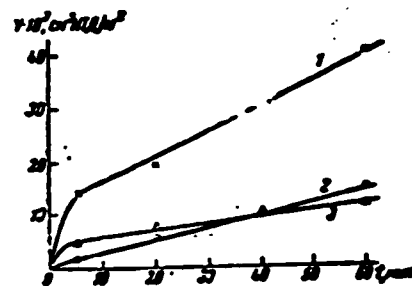1-2a(r'_1,R_5)Cu; 2-(r'_1,R_7)Cu; 3-2b(R_7)Cu 4-2c(Cu); 5-2a(r'_1,R_5) Cu,Zn; 6-2a (r'_2,R_5)Cu.

Fig.2.Catalytic activity of polychelates of 2a structure (R_7,r_1) for metals:
1-Cu; 2-Ni; 3-Co; $T=108°$, p = 1 mm Hg.

In this structure the chelate bond of the metal is formed on account of active groups of polymeric chains, having nitrogen and sulphur atoms, which, entering with the metal into chelate bonds, form a polymer of honeycomb structure. The third type of polymer 2c with the very same chelate unit was obtained on the basis of rubiamo hydrogen acid.

The method of measuring catalytic activity was describes before by [2]. Decom-

poaition of hydrazine was investigated at a hydrazine vapor pressure of 1 mm Hg.

The polymer was first degasified at $110°$ until gas formation has stopped, gas control-

led by the Mc-Leod gage with a constant of $5 \cdot 10^{-5}$ mm^{-1}. Decomposition of hydrazine

was recorded by the pressure rise during the separation of gaseous decomposition pro-

ducts. Hydrazine can decompose by two reactions:

$$1 \ N_2H_4 \longrightarrow N_2 + 2H_2;$$

$$2. 3N_2H_4 \rightarrow 4NH_3 + N_2.$$
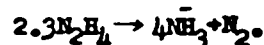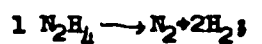
In decomposition products were determined individually nitrogen, hydrogen and

ammonia pressures. On the basis of the composition of gaseous products was calculated

the percentage of hydrazine decomposition by the first and second methods.

In fig. 1 and in table 2 are given data on the study of catalytic activity of bis

(aza-thia)-polychelates of various metals.

Table 2. Catalytic activity bis(aza-thia)-polychelates

(1)Polychelates	(2) S_{spec} m^2/g	(3)Rate of re-action V.10^2	(4) E kcal/mol	(5)K cm^3/kg $m^2 \times min$		Percentage of hydrazine decomposition (6) I-direction / II-direction
1)	2)	3)	4)	5)	6)	7)	
2a (N_a, r_1') Cu	0.07	217	2,7	5,4·10⁻⁶	79	21	
2a (R_a, r_1') Cu	0,10	215	—	—	42	58	
2a (R_a, r_1') Cu	0,24	220	—	—	79	21	
2a (R_a, r_2') Cu	0,238	47	4,8	8·10¹	89	11	
2b (R_q) Cu	0,35	77	2,8	3,8·10²	42	8	
2b (R_a) Cu	1,05	8	—	—	57	43	
2a (R_s, r_1') Cu –	4,34	6	5,0	1,9·10⁴	88	12	
2a (R_a, r_1') Cu, Zn	3,17	6	—	—	61	39	
2aCu	0,50	75	—	—	12	88	
2aNi	0,10	20	—	—	0	100	
2a (R_s, r_1') Co	18,35	3	—	—	8	—	
2a (R_s, r_1') Ni	5,00	1,5	—	—	12	81	
2a (R_1) Pd	2,37	5	7,3	1,8·10⁰	19	81	
2a (R_a, r_2') Ni	0,98	0,0	—	—	—	—	
2a (R_a, r_1') Zn	8,54	0,.	—	—	—	—	
2a (R_s, r_1') Cu	10,40	7	6,9	2·10⁰	80	20	

It is evident, that the highest catalytic activity was displayed by copper polychel-

ate of 2a structure $(R_5, r'_1)Cu$. Replacement of 30% Cu by zinc in the given polychelate

in the process of preparing the polymer reduces specific catalytic activity by 38 times

i.e. by the nonproportionally substituted part of the copper.Zinc compounds of the very same polymer structure were catalytically inactive.

The reproducibility of results was checked on samples of several indi.idual batches. High specific catalytic activity was also possessed by cupper chelate of 2b structure $(R_7)Cu$.

The activity of copper polychelates of 2a structure $(R_5,r)Cu$ drops at the replacement of the R_5 radical by the R_7 by 36 times. This result is reproduced in compounds of various preparation, and the replacement in the polymer of 2a structure (R_5,r'_1) Cu of the pyridine by lutidine with the formation of structure 2a $(R_5,r')Cu$ leads to a 4.5 times drop in activity. Of the investigated copper, nickel, cobalt, palladium and zinc polychelates the activity was demonstrated by copper chelates.In fig.2 are given kinetic isotherms for the decomposition of hydrazine on polychelates of 2a Structure (R_7,v) for Cu, Co, Ni metals. It is evident from the drawing, that metals are situated in the order of decreasing activity in the Cu $\searrow$ Co $\searrow$ Ni series. In polymers of structure 2a (R_5,r'_1) nickel and zinc are inactive. Introduction of palladium instead of copper reduces activity by 10 fold.On polychelates of various metals the change in chemical composition and structure of the polymer produces a different effect. At the change over from the polymer structure 2a (R_7,r'_1) Cu to structure 2a $(R_5,r'_2)Cu$ activity of the polymer rises by 7.5 times, and for nickel polymers it drops by more than 10 times. In this way on different metals the structure of the polymer exerts an irregular effect.

2. Catalytic Activity bis (aza-oxa)-polymer in chelate unit 2 $(N,O)Me$

We investigated the catalytic activity of three types of polymers with mentioned composition of the chelate unit, differing in chemical composition and structure of polymeric chain (see table 1). Polymers,designated further as structure 3a,were obtained during reaction of polymeric Schiff's bases (poly-5,5'-methylene-bis-salicylal dimines, poly-5,5'-methylene-bis-salicylal ethylenediimines, poly-5,5'-methylene

bis-salicylal-hexamethylene diimines, poly-5,5'-methylene-bis-salicylal-phenylene-dii-
mines) with metal salts. In this case were derived polymers of $3a(r)Me$ structure
(radicals r are designated in table 1) with Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Mn^{2+} metals. Poly-
mers with the very same chelate unit bis (aza-oxa)-structure $3b(r)Me$ were obtained
on the basis of diacetylresorcin during its reaction with corresponding metal salts.
In this structure as well as in the previous one the radical r attaches itself to
nitrogen atoms, connected with the metal. The very same radicals have been introduced.
Structure $3c(r)Me$ differed from $3a(r)Me$ by the presence in the polymer of an amido-
diphenyl radical chain analogous to the one which is included in the polymer of struc-
ture 2a. In fig.3 are shown kinetic isotherms of hydrazine decomposition at 108° into
bis (aza-oxa)-polychelate of copper. In table 3 is given a summary of data on cataly-

tic activity of this group of polymers. Cop-
per chelates are arranged in series in the
order of decreasing activity: $3b(r_3)Cu$, $3c$
$(r_2)Cu$; $3a (r_2)Cu$, $3a (r_1)Cu$, $3b(r_2)Cu$. The
rate of catalytic decomposition of hydrazine
increases when radical r_2 is replaced
by r_3 in copper polychelates of 3b structure
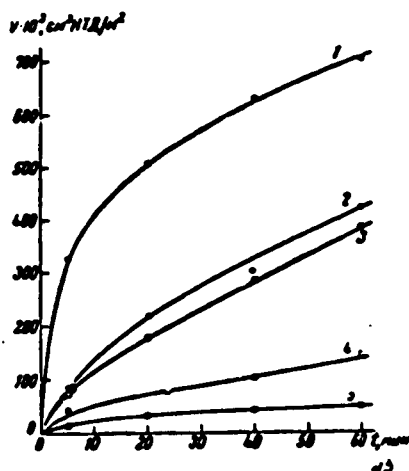at unchanged composition of remaining

Fig.3. Kinetic isotherms of hydrazine de-
composition into bis (aza-oxa) polychelates
of copper of various structure, differing
by the composition of radicals (T=108°,
p = 1 mm Hg): 1-$3b(r_3)Cu$; 2-$3c(r_2)Cu$;
3-$3a(r_2)Cu$; 4-$3a(R_1)Cu$; 5-$3b(r_2(Cu.

polymer by 20 fold. An analogous effect on
catalytic activity is observed for copper
polychelates of $3a(r)Cu$ structure. Replacement
of r_1 radical by r_2 increases the activity
by two times. The structural effect of the polymer with unchanged radical r, attached
to nitrogen atoms, connected with the metal in the chelate unit, is less considerable.
And so for copper polychelates 3a $(r_2)Cu$; $3b(r_2)Cu$ and $3c(r_2)Cu$ the activity changes
in ratio 110:30: 20, i.e. only a by a total of 5 times. Highest catalytic activity
in polymers of structure 3a, 3b and 3c is demonstrated by copper polychelates.

Less active are polychelates of iron. Totally inactive are polychelates of nickel and zinc. In fig.4 is shown the rate of catalytic decomposition of hydrazine in standard conditions at 108° for bis(aza-oxa)-polychelates of copper and iron.

Table 3. Catalytic Activity of bis(aza-oxa)-Polychelates

(1)Polychelate	(2)S_{spec} m^2/g	(3)Rate of reaction $W \cdot 10^3$, cm^3	(4) E kcal/mol	(5)k_0 $cm^3 HTD/m^2 \times min$	Percentage of hydrazine decomposition	
					(6)I direction	(7)II direction
(1)	(2)	(3)	(4)	(5)	(6)	(7)
3a (r_1) Cu	11.20	5	7,3	$2,5 \cdot 10^4$	2	58
3a (r_2) Cu	9,66	10	4,3	$2,8 \cdot 10^4$	37	63
3a (r_3) Ni	2,02	0,0	—	—	—	—
3a (r_2) Ni	1,57	0,0	—	—	—	—
3a (r_3) Ni	4,67	0,0	—	—	—	—
3a (r_1) Fe	7,15	2,0	6,4	$6 \cdot 10^3$	17	83
3a (r_2) Fe	3,81	6,0	3,2	$1 \cdot 10^3$	70	30
3a (r_3) Fe	16,60	0,6	6,0	$5 \cdot 10^3$	43	57
3a (r_1) Zn	0,58	0,0	—	—	—	—
3a (r_3) Zn	9,40	0,0	—	—	—	—
36 (r_2) Cu	0,39	2,0	—	—	66	34
36 (r_3) Cu	0,22	40	—	—	58	42
36 (r_2) Ni	1,31	0,0	—	—	—	—
36 (r_3) Ni	4,9	0,0	—	—	—	—
36 (r_3) Zn	0,93	0,0	—	—	—	—
3в (r_2) Cu	0,40	10	—	—	54	46
3a (r_1) Mn	11,3	6	—	—	31	69

Catalytic activity of copper polychelates is considerably higher. In the drawing is shown the activity of iron catalysts,obtained as result of developing a catalyst (initial activity lower). For iron polychelates the presence of radical r_2 is also connected with much higher activity as compared with r_1 and r_3. Activity changes in ratio 6:2:0.6.
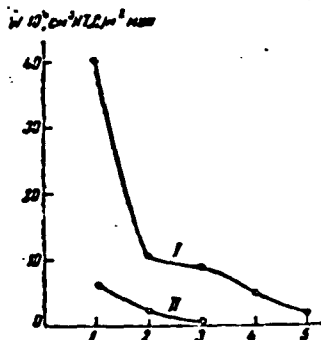

Fig.4

Fig.5

Fig.4.Dependence of specific rate of decomposition of hydrazine on bis(aza-oxa)-copper polychelates (curve I) and iron polychelates (curve II) of various structure
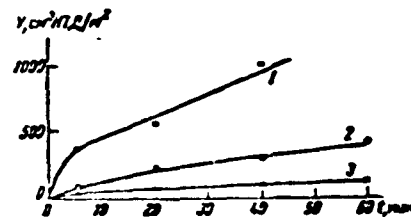
and chemical composition: 1-1-3b(r_3)Cu; 2-3b(r_2)Cu; 3-3a(r_2)Cu; 4-3a(r_1)Cu; 5-3b (r_1)Cu; II-1-3a(r_2)Fe; 2-3a(r_1)Fe; 3-3a(r_3)Fe; T = 108°; P = 1 mm Hg.

Fig.5.Kinetic decomposition isotherms of N2H$_4$ into bis(di-oxa)-copper polychelates 1-4c(Cu); 2-4b(Cu); 3-4a(Cu); T= 108°, P=1 mm Hg.

The polymer, consisting manganese in the structure 3a(r_1)Mn has a catalytic activity close to the activity of iron polychelate 3a(r_2)Fe.

3. Catalytic Activity of bis(di-oxa)-polymers with chelate unit 2(O,O)Me.

We investigated the catalytic activity of bis(di-oxa)-polymers of three structures (see table 1).

In fig.5 are presented kinetic isotherms of hydrazine decomposition on three types of bis(di-oxa)-copper polychelates. It is evident,that maximum activity is displayed by the sample of structure 4c(Cu). Specific catalytic activity of the sample of structure 4c(Cu) exceeds by 4 times the activity of sample structure 4b(Cu). Polymer of structure 4a(Cu) has a much lower activity. It is characteristic,that polymers containing iron and nickel, in structure 4c (table 4)have the low catalytic activity, while in structure 4a they are totally inactive. Specific catalytic activity of polymers in the series 4c(Cu), 4c(Fe), 4c(Ni) at 108° is expressed by the ratio (44: 3:1) 10^{-3} cm^3/m^2.min.

Table 4.Catalytic activity of bis-(di-oxa)-polychelates

(1) Polychelate	(2) S_{spec} m²·ATD/g	(3) W·10^3 cm³/m²·min (T=108°)	(4) Percentage of hydrazine decomposition I direction	(5) II direction
(1)	(2)	(3)	(4)	(5)
4a (Cu)	0,50	5	86	14
4a (Fe)	0,53	0,0	—	—
4a (Ni)	4,96	0,0	—	—
46 (Cu)	1,05	12,0	0	100
4a (Cu)	3,04	44,0	87	13
4в (Fe)	3,53	1,0	0	100
4a (Ni)	4,82	3,0	0	100

4. Effect of structure and chemical composition of polymer on selectivity

Up until now we accented our attention on the total rate of hydrazine decomposi-

tion, omitting the trend of the decomposition. The trend of the decomposition char-
acterizes a very important property of the catalyst - its selectivity. As was shown
by an investigation of   polychelates with different composition of the chelate-
. unit and the organic radicals included in the polymer, selectivity, as well as the
rate of decomposition,are very sensitive to the structure and chemical composition
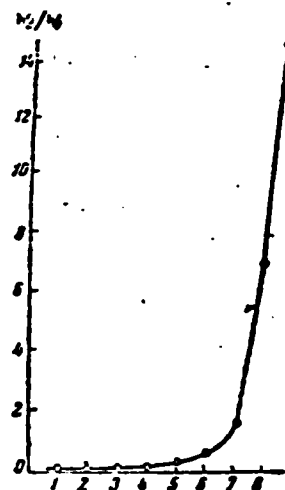of the chelate unit and organic part of the molecule as well.

Selectivity can be evaluated by the ratio o'r rates of hydrazine decomposition
by the first and second method.

To investigate copper polychelates the decomposition trend changes from 100%-
decomposition by the first reaction into nitrogen and hydrogen for certain polymers
of structure 2 and 1 with chelate unit 2 $(N,S)Cu$ and $(S,S)Cu$ to 100% decomposition
into nitrogen and ammonia by the 2-nd reaction for copper polychelates of structure 3
with chelate unit $2(N,C)Cu$ and structure 4b with chelate unit $2(0,0)Cu$. When changing
the organic part of the polymer by introducing radicals R and r of various structure,
the ratio of rates of decomposition of hydrazine in the first in second reactions
and the selectivity have an intermediate value.

In fig.6 is given the dependence of selectivity of the investigated copper poly-
chelates upon their chemical composition and structure. Along the axis of the ordinates
are plotted ratios of rates in accordance with second and first reactions W_2/W_1. On
the axis of the abscissa to the left are situated compounds leading the decomposition
into nitrogen and hydrogen, to the right - leading decomposition into ammonia and
nitrogen. The ratio of rates of decomposition W_2/W_1 on certain polymers changes with
temperature,which indicates a difference in activation energies of those two decom-
position processes. Such a change took place in $2b(Cu)$ and $2a(R_5,r'_2)Cu$ compounds.
With the rise in temperature the percentage of decomposition by the first reaction
increased in both instances ,which indicates a much higher activation energy of de-
composition by the first reaction. Activation energies,calculated for the decomposi-

tion by first and second reactions on the compound $2a(R_5,r'_2)Cu$, equal 5.7 and 0.6
ckal/mol resp. On compounds $3a$ $(r)Cu$ decomposition in the entire investigated range
of temperatures takes place in accordance with second reaction. On the polymer $2a(R_7)Cu$
the ratio of the rate of decomposition w_2/w_1 in the interval of $26-108°$ remains con-
stant, indicating approximate equality in activation energies of both processes.

An analogous dependence of selectivi-
ty upon composition is also observed for
nickel polychelates. And so, for example,
on a nickel polychelate of structure $2b$
with chelate unit $2(S,S)Ni$ the decomposi-
tion of hydrazine in the investigated range
of temperatures occurs by second reac-
tion. On a nickel polychelate of previous-
ly investigated structure 1 with chelate unit
$2(S,S)Ni$, the rate of decomposition by
first and second reactions are commensu-
rate, their ratio changes smoothly in de-
pendence upon the organic radical, which

Fig.6.Selectivity of catalytic decomposi-
tion of hydrazine by first and second re-
actions for copper polychelates of various
structure and chemical composition:
$1-1(R_4)Cu$; $2-1(R_5)Cu$; $3-3b(r_2)Cu$; $4-2b(r'_1)$
Cu; $5-2b(r'_1)(R_5)Cu$; $6-3b(r_2)Cu$; $7-3a(r_2)$
Cu; $8-2c(Cu$; $9-3b(r_1)Cu$.

is included in the polychelate. In this way,the selectivity of the reaction sensitive
to chemical composition of the chelate unit, as well as to structure and composition
of organic radicals of the polymer can be regulated in broad limits by changing se..e.

5. Comparing catalytic activity of polychelates with catalytic activity of corresponding monomers.

When studying metalloorganic chelate polymers a problem arises on whether
the specifically observed laws of catalytic activity for polymers are not determined
by the effect of atoms very close to the metal and whether the complex compounds will
be of the very same composition,i.e.monomeric analogues of investigated polymers,
and possess analogous properties. To explain this problem was measured the specific

catalytic activity of monomeric analogues, representing one link in the series of

polychelates listed in table 1. The structure of the investigated complex compounds

- monomers, their specific catalytic activity and catalytic activity of corresponding

polymers are listed in table 5.

Of the series of monomers listed in table 5 for the three first ones correspon-

ding polymers were distinguished by high catalytic activity. The investigated corres-

ponding monomers were found to be in analogous conditions catalytically inactive.

Table 5. Comparing catalytic activity of polymers with activity of corres-
ponding monomeric analogues

Composition of monomer (1)	(2)	Abbrev.desig- nation of monomer	S_{spec} m^2/g (3)	$W \cdot 10^3$ $\dfrac{cm^3}{m^2 \cdot min}$ (4)	Polymer (5)	S_{spec} m^2/g (6)	$W \cdot 10^3$ $\dfrac{cm^3}{m^2 \cdot min}$ (7)

(See page 12 a for Table 5)
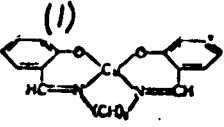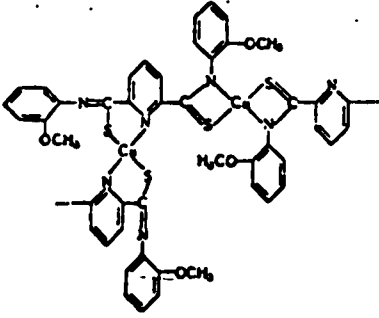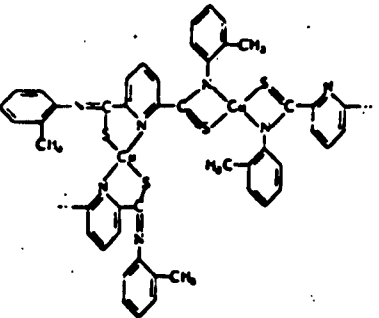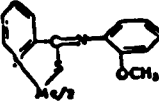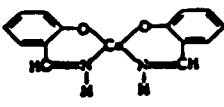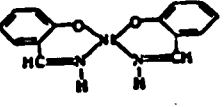
(1)	(2)	(3)	(4)	(5)	(6)	(7)
	СИМ-2	0,66	0,00	3a (r₂) Cu	0,66	12,00
	2619Cu	0,53	0,00	26 (R₁) Cu	0,35	80,00
	2618Cu	0,56	0,00	26 (R₄) Cu	1,05	8,00
	2a19Cu	0,32	0,00	2a(R₇,r₁)Cu	4,34	6,00
	СИМ-1	0,7	30,00	3a (r₁) Cu	11,2	5,00
	СИН	0,97	0,00	3a (r₁) Ni	2,02	0,00

Table 5

One of the monomers—copper salicylalimine, representing a monomeric analogue of a less active polymer $3a(r_1)Cu$, had at $108°$ a specific catalytic activity,close to the catalytic activity of corresponding polymer $3a(r_1)Cu$.

Estimation of results

We investigated polychelates bis(aza-thia), bis(aza-oxa), bis(dioxa) and a previously investigated system of di-thia ([2]) polychelates, the composition of the chelate units of which can be presented conditionally as $2(N,S)Me;2(N,0)Me; 2(0,0)Me$ and $2(S,S)Me$. In the latter case for copper polychelates the chelate unit had a structure $Cu(S,S)$ as result of the monocharge state of the copper.In all remaining structures of polychelates the copper was in bivalent state.

Investigation of hydrazine decomposition showed,that the catalytic activity of polychelates depends strongly upon the chemical nature of the atoms, connected with the metal in chelate unit.In fig.7 is shown the change in rate of decomposition of hydrazine at $108°$ on copper poly-chelates with various composition of addenda atoms in the chelate unit in dependence upon the nature of organic radicals,included in the polymer. Polymers are arranged in the order of reducing their catalytic activity. It is evident from
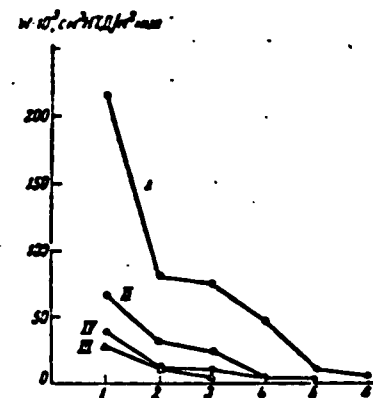

Fig.7.Rate of decomposition of hydrazine on copper polychelates,characterized by composition of chelate unit,in relation to composition or organic radical of polymer:
$1-2(N,S)Cu - 1 - 2a(r'_1,R_5)Cu, 2-2b(R_7)CU;$
$3-2c(Cu), 4-2a(r'_2,R_5)Cu,^5 50 2b(R_6)Cu,$
$6-2a(r'_1,R_7)Cu; II - (S,S)Cu-1-1(R_2)Cu,$
$2-1(R_3)Cu, 3-1(R_5)Cu, 4-1(R_7)CU; III-2(0,0)$
$Cu-1-rc(Cu), 2-4b(Cu), 3-4a(Cu). IV-2(No)$
$Cu-1-3b(r_2)Cu, 2-3c(r_2)Cu, 3-3a(r_2)Cu,$
$4-3a(r_1)Cu, 5-3b(r_2)Cu.$

the drawing that highest reactivity is possessed by bis (aza-thia)copper polychelates bis(aza-thia), followed by di-thia copper polychelates, of which only one had an activity, comparable with the mean activity of aza-thiacopper polychelates. The catalytic activity of series bis (di-oxa)- and bis (aza-oxa)-copper polychelates is close. In this way, inspite of the fact,that the introduction of various organic radicals

into the basis and side chains of the polymer exerts a stron effect on catalytic activity, by changing same in broad limits. copper polychelates,depending upon the composition of the chelate unit can be arranged inseries : $2(N,S)Cu > (S,S) Cu > 2(N,O)Cu; 2(O,O)$ Cu.

For nickel polychelates was derived a similar dependence of activity upon the structure of the chelate unit.The highest catalytic activity was discovered for nickel polychelates in structure 1 and 2 with chelate unit $2(S,S)Ni$ and $2(N,S)Ni$. In structures 3 and 4 with chelate units $2(N,O)Ni$ and $2(O,O)Ni$ respectively, nickel poly- chelates are catalytically inactive. Only one polymer of structure 4e (Ni) had weak catalytic activity. The copper polymer of the very same structure 4c(Cu) is 44 times more active. Attention is attracted by the fact that bis(aza-thia)-nickel polymers are less active,than bis(di-thia)-polymers.For copper polychelates we have a reverse dependence. It is possible, that this difference is connected with the fact,that the copper in these compounds, in contrast to Ni, is not in an identical valent state.

Summarizing,it is possible to mention the following laws, revealed in the cata- lytic activity and selectivity of chelate polymers.

1. Catalytic activity and selectivity are determined by the metal included in the polychelate.

2. The second factor,determining catalytic activity and selectivity is the nature of addenda atoms, connected with the metal in the chelate unit.

3. The third factor appears to be the nature of organic radicals,included in the polymer.

4. Monomeric analogues of the polychelate series are catalytically considerably less active than the corresponding polychelates.

5. Maximum catalytic activity of nickel and copper polychelates in reactions of hydrazine decomposition exceed the catalytic activity of oxides and sulfides of the very same metals by two and more orders.

A comparison of electro econductivity and catalytic activity of individual poly-

chelates does not give any indications for the presence of any king of interrelation between same.

And so for example, zinc polychelates of structure 1, as well as copper ones, have an electrical conductivity of 10^{-9} (ohm. cm) $^{-1}$, nickel polychelates have an electrical conductivity of less than 10^{-13} (ohm. cm)$^{-1}$ (6). Catalytic activity of nickel and copper polychelates is high, and zinc polychelates are catalytically inactive.

The absence of connection with electrical conductivity is, apparently, connected with the fact, that the basic nature of chemosorption and catalysis are determined not by the semiconductor properties of the polymer as a whole, but by the electron state of the metal in chelate unit. This circumstance, apparently, is due to the detected sharp influence of the nature of addenda atoms, included in the chelate unit on tho catalytic properties of the polymer. The high catalytic activity, disclosing exclusively by chelate polymers of transient metals, make it possible to include in the interpretation the results of the crystalline field theory (7). But these considerations do not include the high catalytic activity of polychelates of monovalent copper in structure 1, which does not have free d-levels. Catalytic activity of polychelates containing divalent copper, exceeds the catalytic activity of polychelates of structure 1, in which the monovalent state of copper has been proven.

At present there is still no clear idea about the mechanism of electro-conduction and the nature of conductivity of the investigated polychelates. It is possible, that in polychelate of structure 1 is present a certain number of divalent copper ions. In this case the contradiction can be eliminated. Data on the effect of chemical adsorption of hydrazine on the electro conduction of copper polychelates of structure 1 speak in favor of the electron nature of conductivity of these polymers. Adsorption of hydrazine cause a reduction in resistance, i.e. rise in electro conductivity. Hydrazine, being adsorbed on nickelous oxide, reveals electron donor qualities. It may be thought, that adsorbing on polychelates, it also remains a donor. The oxygen as a rule, during adsorption reveals exclusively acceptor properties, becoming

negatively charged. The entry of oxygen produces no change in resistance in a majority of polychelates, attesting to the absence of oxygen adsorption on them. In few cases as for example, for the $1(R_4)$Cu polymer the entry of oxygen at $120°$ is followed by a rise in polychelate resistance from $3.7 \cdot 10^8$ to $4.5 \cdot 10^8$ ohms, which decreases again when the oxygen is removed by pumping. Oxygen and hydrazine, as they are adsorbed, change the resistance of this polychelate in opposite direction.

Such nature of change in electrical conductivity at the time of hydrazine and oxygen adsorption is characteristic for semiconductors with electron conductivity. At present time is being conducted and investigation for the purpose of explaining the nature of electrical conductivity of the investigated polychelates.

Interesting is the effect of the organic part of the polymer on catalytic properties. Replacement of some organic radicals by others leads to a change in the properties of the polymer, especially, its thermo stability, which points toward a deep change in the chemical bonds, which take place in the polymer [8]. And so for example, for polymer 2b (R_7)Cu the loss in weight when heated to $370°$ is 39%, for the polymer 2b (R_6) Cu - 28.0%, and for 2b(R_5)Cu - only 12.5%, i.e. the strength of the polymer φ changes at a change in polymers of structure 2a and 2b of radicals in magnitude $\varphi (R_5) > \varphi (R_6) > \varphi (R_7)$; catalytic activity of the polymer 2a(R_5, r'_1) Cu is greater than the catalytic activity of the 2a(R_6, r'_1)Cu polymer.

The effect if polymer structure on the selectivity of hydrazine decomposition reaction, is of principle interest.

Decomposition in two directions (by two tendencies), is possibly, connected with two entirely different mechanisms of these processes. It is not clear now, whether decomposition takes place on various sections or on one and the very same ones and what the nature of these sections is. To explain all these questions the mechanism of decomposition is being investigated. The revealed laws have an analogy with the laws determining the properties of ferments. Chelate polymers belong to the new type of heterogeneous catalysts, intermediate between ordinary inorganic catalysts and natural

highly active catalysts - ferments. Explanation of the catalysis mechanism by such contact ideas is of principal interest for the theory of selecting catalysts.

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